UDC 666.3/.7:661.883

BIOCERAMIC BASED ON ZIRCONIUM DIOXIDE

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Translated from *Steklo i Keramika*, No. 4, pp. 25 – 28, April, 2009.

A bioinert ceramic based on partially stabilized tetragonal zirconium dioxide has been developed and its chemical and phase composition, microstructure, and physical – technical properties have been investigated. Ceramic heads for endoprostheses for the coxofemoral joint — 28 mm in diameter with less than 0.02 μm roughness R_a of the spherical surface and 1 μm deviation from sphericity — have been fabricated. It is shown that the bioceramic which has been developed and the ceramic heads for endoprostheses fabricated from it meet the technical characteristics and parameters required by international standards and their quality is at least as good as that of the analogous articles manufactured by well-known firms.

Key words: zirconium dioxide, microstructure, bioceramic, endoprosthesis

Ceramic based on the tetragonal modification T-ZrO_2 of zirconium dioxide is now one of the strongest and inert ceramic materials available. This makes it possible to use T-ZrO_2 in orthopedics, just like aluminum oxide (Al_2O_3) based ceramic, for complete coxofemoral endoprosthetization as the head (ball component) of the endoprosthesis in a rubbing couple with polyethylene materials., The ZrO_2 based ceramic differs from Al_2O_3 based ceramic by high strength and fracture toughness, which is especially important for the head of an endoprosthesis because of tensile stresses arising with the conical fitting of the head on the foot of the endoprosthesis.

ZrO_2 based ceramic heads fpr endoprostheses have been in use since 1985 [1]. Over the years more than 400,000 coxofemoral endoprostheses with ZrO_2 ceramic heads have been implanted. Most of them were fabricated from yttrium oxide Y_2O_3 stabilized tetragonal polycrystalline zirconium dioxide with the composition (molar content) 97% ZrO_2 + 3% Y_2O_3 (Y-TZP). The five best-known manufacturers of ZrO_2 ceramic heads for coxofemoral endoprostheses are: "Kyocera" and NGK in Japan and "Morgan-Matroc" (England), "Metoxit" (Switzerland), and "Norton-Desmarquest" ("Prozyr Heads") (France) in Europe.

The main requirements for Y-TZP based ceramic materials used for manufacturing surgical implants are given in the international standard ISO 13356–1997. These materials must be, first and foremost, highly pure and homogeneous with respect to chemical and phase compositions, have a high-density uniform fine-grain structure, and be quite strong.

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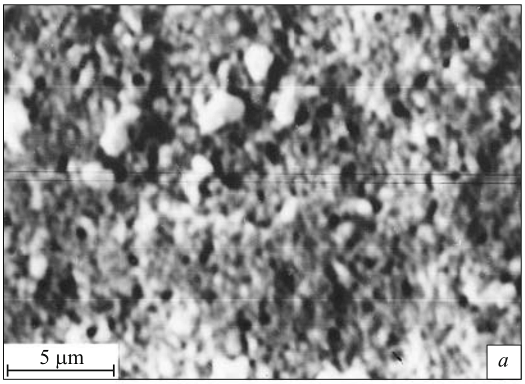
A bioinert ceramic based on T-ZrO_2 has been developed at the I. N. Frantsevich Institute of Materials Science (IMS) from nanocrystalline powders. Complex stabilization of the zirconium dioxide by yttrium and cerium oxides (Y, Ce-TZP) is used to increase the strength of the ceramic materials. The bioceramic material developed has been used to manufacture the ceramic heads of coxofemoral endoprostheses.

The chemical composition of the synthesized nanocrystalline powders and bioceramics was determined by chemical and spectral analyses. X-ray investigations were performed with a DRON-1,5 diffractometer (CuK_α radiation, scan rate 1 – 4 °/min). Electron-microscopic studies were performed with a Camebax SX-50 microprobe. The specific surface area of the nanocrystalline powders was determined by the method of thermal adsorption of nitrogen (BET). The density of the bioceramics was determined by hydrostatic weighing.

The strength of the bioceramics was determined by the three-point bending method (NIK IMP 1231-U10 universal machine for performing mechanic tests with the experimental data recorded automatically). The tests were performed on small (3.5 × 5.0 × 50.0 mm) polished rectangular blocks. The sharp edges of the blocks were blunted. The roughness R_a of the spherical surface of the ceramic heads was determined with a TALYCUPF 5M-120 profilometer-profilograph.

Wear tests were performed by the pin-disk scheme [2] under the following conditions: constant load — 5 MPa; slip rate — 0.1 m/sec; medium — Ringer's solution containing 9 g/liter NaCl (physiological solution); testing time — 20 h with the results recorded every 5 h. The stationary pin was made of polyethylene and the rotating disk (counterbody)



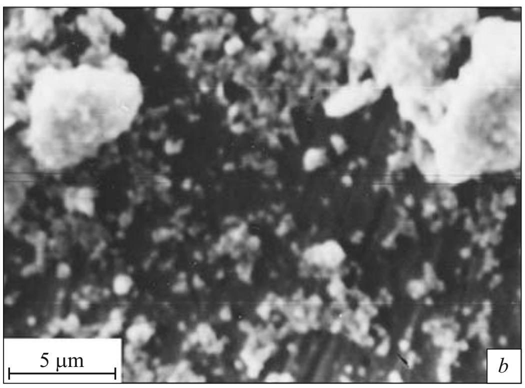


Fig. 1. Morphology of nanocrystalline powder: *a*) M-ZrO_2 after hydrothermal decomposition in an acid medium at 170°C for 6 h; *b*) metastable T-ZrO_2 after mechanical – chemical treatment and calcination at 600°C for 2 h.

was made of material which is used as part of rubbing couple to determine the wear of polytethylene. The wear of polyethylene was calculated from the decrease of the volume of the polyethylene pin as a result of rubbing; for this, the dimensions of the pin were measured to within 1 μm, before and after the tests, using an IK-6 vertical optimeter. The wear of the disks was also determined (according to the mass).

Two methods were used in succession to synthesize the initial Y, Ce-TZP nanocrystalline powders: hydrothermal decomposition of zirconium salt in an acidic medium and mechanical working of the obtained powder and alloying additions [3, 4]. Chemically pure zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$, yttrium nitrate $Y(NO_3)_3 \cdot 6H_2O$, and cerium nitrate $Ce(NO_3)_3 \cdot 6H_2O$ were used as the initial materials.

High-purity hydrous ZrO_2 nanocrystalline powder, containing up to 2% hafnium dioxide HfO_2 as the natural impurity, was synthesized at the first stage. For this, a water solution of zirconium oxychloride with a definite concentration was treated under hydrothermal conditions at 170 – 190°C for 6 h [3]. An advantage of the hydrothermal decomposition in an acid medium over other methods of obtaining ZrO_2 nanocrystalline powders is homogeneity of the process of nucleation and growth of the primary particles. A monoclinic

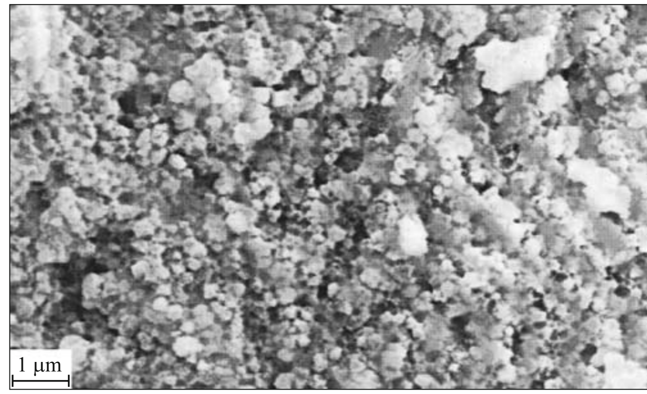


Fig. 2. Microstructure (fractogram) of ZrO_2-based bioceramic.

modification of zirconium dioxide M-ZrO_2 was obtained from the synthesis process.

During mechanical – chemical treatment dried M-ZrO_2 nanocrystalline powder was permeated with water solutions of yttrium and cerium nitrate solutions taken in the required quantity, homogenized in a planetary mill (2 h), and calcined in air at 600°C for 2 h. To prevent intense release of water vapor and nitrogen oxide as well as loss of powder particles the temperature in range 20 to 200°C in the furnace was raised at a rate no exceeding 1°C/min, after which the temperature increase was arbitrary, and the mixture was allowed to cool down together with the furnace. A metastable tetragonal solid solution of zirconium dioxide Y, Ce-TZP in which the M-ZrO_2 content did not exceed 5 – 7%[2] formed during heat treatment of the mixture. The specific surface area of the powders was in the range 72 – 75 m^2/g.

The morphology of the powder obtained is displayed in Fig. 1. Nanocrystalline M-ZrO_2 powder consists of individual rounded agglomerates with average size up to 0.5 μm, though individual agglomerates reach 1 – 2 μm (see Fig. 1*a*). After the mechanical – chemical treatment the agglomerates retain their shape, but their average size increases to 1 μm. Individual agglomerates up to 5 μm are encountered (Fig. 1*b*).

Uniaxial cold pressing followed by cold isostatic pressing under pressure 150 – 200 MPa was used to make blanks of samples and ceramic heads for coxofemoral endoprosthesis [5]. The blanks were sintered in air at 1320 ± 20°C for 2 h in a regime with temperature increasing and decreasing slowly. The sintered blanks were mechanically worked using abrasive and diamond tools as well as diamond pastes and powders following the method presented in [6].

A study of the composition of the sintered bioceramics showed that this material based on ZrO_2, Y_2O_3, CeO_2, and HfO_2, which together comprise more than 99%, has the following composition: Y_2O_3 from 4.5 to 5.4%; CeO_2 3.0%, HfO_2 no more than 2%; the main impurity is Al_2O_3 (no more than 0.5%). According to the phase composition this is a tetragonal solid solution based on ZrO_2 (T-ZrO_2); the content of the monoclinic phase is no more than 3%. The microstructure of the material is displayed in Fig. 2. It is evi-

[2] Here and below — content by weight.

TABLE 1.

Test duration, h	Wear of polyethylene paired with different materials, cm^3			
	VT6 alloy	CoCrMo alloy	Al_2O_3 based bioceramic	ZrO_2 based bioceramic developed
5	0.0160	0.0017	0.0003	0.0002
10	0.0260	0.0020	0.0013	0.0012
15	0.0320	0.0022	0.0021	0.0018
20	0.0390	0.0027	0.0026	0.0022

dent that sintering produced a high-density, uniform, fine-grain structure with average grain size of the order of 0.4 μm. The density of the bioceramics obtained is 6.01 – 6.03 g/cm^3, and the maximum bending strength is at least 600 MPa.

The results of wear measurements performed on "Chirulen" high-density polyethylene are presented in Table 1. Practically all manufacturers of joint endoprostheses use this material in the moving mobile joint and in rubbing couples with the ZrO_2 based bioceramic developed and other materials used for the heads of the endoprosthesis: the titanium alloy VT6 (GOST 19807–91), the alloy CoCrMo [7], and Al_2O_3 based bioceramic [6].

As the data in Table 1 show, the wear of "Chirulen" polyethylene rubbing couple with the ZrO_2-based ceramic developed is an order of magnitude lower than in a couple with the titanium alloy VT6 throughout the entire duration of the tests. For rubbing couples based on the alloy CoCrMo and the Al_2O_3-based ceramic, the wear of polyethylene coupled with ZrO_2-based ceramic during the first 5 h of the tests is approximately 6 – 9 times lower, and as the test duration increases, this ratio decreases and wear becomes practically comparable.

Analysis of the state of the rubbing surfaces of the polyethylene pin and the disks after the tests showed that in pairs where the lowest wear of polyethylene was observed (bioceramics, CoCrMo alloy), roughness close to the initial level remained in both contact surfaces, while the wear process for the titanium disk (VT6 alloy) was accompanied by blackening of the rubbing track and a considerable increase of the surface roughness. At the end of each cycle of the tests, i.e., every 5 h, the wear of the VT6 alloy disk was found to be in the range 5 – 8 μm. The wear of the ceramic disks and cobalt-chromium alloy disks did not exceed the measurement error.

It should be noted that because of the low antifriction properties of titanium alloys most manufacturers of coxofemoral joint prostheses now replace titanium heads with cobalt-chromium or ceramic (based on Al_2O_3 or ZrO_2) heads, which have higher tribomechanical characteristics.

The structure of a ceramic head was developed taking account of the requirements of the international standard ISO

TABLE 2.

Parameter	IMS head	ISO 13356–1997, ISO 7206-2:1996	Head manufacturer	
			"Norton Desmarquest"	"Metoxit"
Ceramic based on oxides	ZrO_2, HfO_2, Y_2O_3, CeO_2	ZrO_2, HfO_2, Y_2O_3	ZrO_2, HfO_2	ZrO_2, HfO_2
Chemical composition, %:				
base:	> 99	> 99	> 99	> 99
HfO_2				
Y_2O_3	< 2	< 5	< 2	< 2
CeO_2	4.5 – 5.4	4.5 – 5.4	5.1 ± 0.25	5.3
impurities:	3.0	–	–	–
Al_2O_3	< 0.5	< 0.5	< 0.5	< 0.005
other oxides	< 0.5	< 0.5	< 0.5	< 0.03
Phase composition	T-ZrO_2	–	T-ZrO_2	T-ZrO_2
Monoclinic phase content, %	< 3	–	< 1	< 5
Density, g/cm^3	> 6.00	> 6.00	> 6.08	6.08
Strength, MPa	> 600	> 500	> 600	890
Grain size, μm	< 0.4	< 0.6	< 0.5	< 0.5
Diameter, mm	28	–	28; 32	28; 32
Tolerance for diameter, mm	– 0.02	– 0.02	– 0.02; 0.04	– 0.01; 0.02
Deviation from sphericity, μm	1	< 10	1	0.1
Roughness R_a, μm	< 0.020	< 0.020	< 0.005	0.005
Fitting cone	12/14	–	12/14	12/14

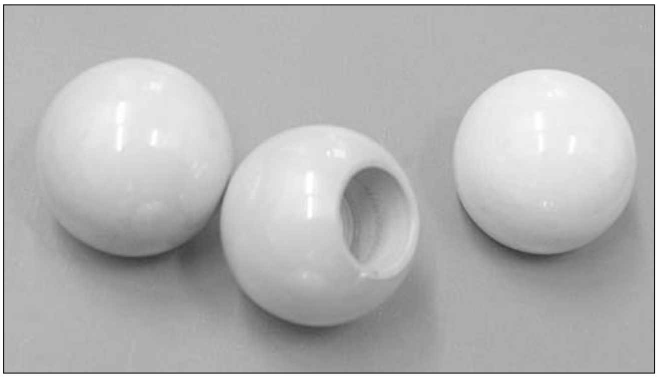


Fig. 3. ZrO_2-based ceramic heads developed for coxofemoral joint endoprostheses.

7206-2:1996. The head has a spherical outer working surface, a base, and a fitting opening under the foot neck. The optimal structural parameters of the head were determined by computer simulation [8], as a result of which heads with the following dimensions were manufactured: outer diameter — 28 – 0.02 mm, height — 24 – 0.3 mm, diameter of the fitting opening — 13.0 + 0.03 mm, fitting cone — 12/14.

Mechanical working makes it possible to manufacture ZrO_2-based ceramic heads with roughness R_a of the spherical surface less than 0.02 μm and deviation from sphericity 1 μm, which is difficult to ensure during finishing of metal heads.

Roughness R_a of the Spherical Surface of Finished Ceramic Heads of Coxofemoral Joint Prostheses Based on Zirconium Dioxide

Ceramic head of surface, μm	Roughness R_a
1	0.016, 0.012, 0.019, 0.010
2	0.012, 0.013, 0.011, 0.015
3	0.012, 0.016, 0.019, 0.015
4	0.015, 0.019, 0.012, 0.015

The values obtained correspond to the requirements of the standard ISO 13356–1997. The ceramic endoprosthesis heads manufactured are displayed in Fig. 3.

The parameters and characteristics of the ceramic heads developed and the ceramic endoprosthesis heads manufactured by the Swiss company "Norton Desmarquest" and the French company "Metoxit" as well as the requirements of the international standards ISO 13356–1997 for ZrO_2 based ceramic for bone implants and ISO 7207-2:1996 for ceramic heads for endoprostheses are presented in Table 2.

In summary, the zirconium dioxide based bioceramics developed makes it possible to manufacture for endoprostheses heads whose technical characteristics and parameters correspond to the requirements of the international standards and are not inferior to the analogous articles manufactured by foreign companies.

The wear of high-density "Chirulen" polyethylene in a rubbing couple with the new bioceramic is considerably lower than in couples with titanium alloy and comparable to the bioceramic based on aluminum oxide and cobalt-chromium alloy, now used in rubbing couples in endoprostheses.

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